

## PATENT ABSTRACTS OF JAPAN

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### (54) REFINING METHOD OF FULLERENE C60

#### (57)Abstract:

**PURPOSE:** To provide a refining method of fullerene C60 with simple operation and process, high space time yield which is significantly and practically useful and easily applied for mass production in an industrial scale so that high purity fullerene C60 is efficiently separated and recovered from soot containing fullerene C60 obtd. by arc discharge of carbon such as graphite or the like or laser abrasion or from a soln. containing fullerene C60 with impurities obtd. by extraction of the soot above described with an org. solvent.

**CONSTITUTION:** A soln. containing fullerene C60 with impurities obtd. by extraction of soot containing fullerene C60 with an org. solvent is subjected to contact treatment with activated carbon. The fullerene C60 is refined by separating and removing the org. solvent from this treated liquid.

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**CLAIMS**

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[Claim(s)]

[Claim 1] The purification approach of the fullerene C60 characterized by carrying out separation clearance of the organic solvent from the obtained processing liquid after carrying out contact processing of the solution which contains with an impurity the fullerene C60 extracted with the organic solvent from the soot containing fullerene C60 with activated carbon.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Industrial Application] When this invention is said in more detail about the purification approach of fullerene C60, it relates to the practically remarkable purification approach of the useful fullerene C60 which can carry out separation recovery of the fullerene C60 of a high grade efficiently from the solution of the crude fullerene C60 obtained by extracting the soot which contains the fullerene C60, such as soot obtained by arc discharge, laser ablation, etc. of graphite, for example, or this fullerene C60 content soot with an organic solvent.

[0002] in addition, the purification fullerene C60 obtained by the approach of this invention -- as an electrical conducting material, the raw material of a super-conductor, etc. -- the electrical and electric equipment and the electronic ingredient field -- for the first time -- \*\* -- it can use suitable for various kinds of fullerene C60 fields of the invention to carry out.

[0003]

[Description of the Prior Art] Recently, the molecule-like carbon matter new type called the carbon cluster (spherical macromolecule) of the closed shell structured type of carbon numbers 60 and 70 and 84 grades is compounded, and attracts attention. The carbon cluster which has this special structure is also called fullerene, and is called fullerene C60, this C70, this C84, etc. by the carbon number which constitutes that molecule frame (only called C60, C70, and C84 grade.). Such fullerene is new carbon materials, and since it is expected that unique physical properties will be shown also from having the special molecular structure, research on the property and application development is advanced briskly. For example, the expectation of fullerene as an electrical conducting material of a high property which the application as lubricant in molecular levels, such as being a spherical macromolecule, is expected, and replaces a graphite etc. since it is the huge carbon molecule of the partial saturation nature of a uniform carbon number is also great.

[0004] In the fullerene of the carbon number of these various kinds, fullerene C60 is the easiest to compound, and its expectation is great also in respect of an application. If a potassium is doped very much to fullerene C60 recently, it is found out that absolute-temperature 18K become a superconductor, a high temperature superconductor is obtained one after another by addition of alkali metal, such as a rubidium and caesium, things are also shown, and attention of since various is actually attracted [Nature, 350,320-322 (1991), Nature, 350,600-601 (1991)].

[0005] Thus, fullerene C60 has the very great expectation as an exotic material and new materials in various kinds of fields of the invention including the electrical and electric equipment and the electronic field, and, so, development of the technique of producing the thing of a high grade to a large quantity as much as possible is desired.

[0006] By the way, although generating these fullerene easily by carbonaceous arc discharge (resistance heating method) and laser ablation (laser evaporation method), such as graphite, is known, the soot which carries out little content of the fullerene is obtained in that case. Then, the technique which carries out separation (concentration) purification of the fullerene

from this soot-like matter becomes important. As a manufacturing technology of the conventional fullerene including this separation / purification approach, from the soot obtained by the above-mentioned approach, extraction separation is carried out with aromatic hydrocarbon, such as benzene and toluene, it carries out to crude fullerene, and the approach a neutral alumina column etc. carries out isolation purification according to chromatography separation using this is learned further [Nature, 347,354-358 (1990)]. Here, aromatic hydrocarbon is used for the extract of fullerene because it is advantageous in respect of the solubility over fullerene etc.

[0007] However, it is difficult to fully obtain the fullerene of a high grade only by an aromatic series solvent etc. extracting from this soot-like matter. In the extract obtained although fullerene C60 could be efficiently extracted when organic solvents, such as aromatic hydrocarbon, actually extracted the soot containing fullerene C60, various impurities contain besides fullerene C60, and the fullerene C60 of a high grade cannot be obtained from this solution only by carrying out separation clearance of the solvent as it was.

[0008] Then, in order to obtain the fullerene C60 of a high grade, separation purification of the crude fullerene C60 (the solution and fine particles containing fullerene C60 and an impurity) conventionally obtained with the extraction method as mentioned above was carried out by the column chromatography method, and the approach of obtaining the fullerene C60 of a high grade was adopted. However, in the purification method by such column chromatography, although it is easily applicable to little purification, there is a not practical trouble in the object which obtains the refined material of a large quantity. So, development of the industrial purification method which can be mass-produced was easily expected the fullerene C60 of a high grade strongly from the solution of the crude fullerene C60 obtained by the soot containing the fullerene C60, such as the above-mentioned soot, or its organic solvent extract.

[0009]

[Problem(s) to be Solved by the Invention] This invention is made in view of the above-mentioned situation. The object of this invention the fullerene C60 obtained by the extract by the soot containing the fullerene C60, such as soot obtained by the arc discharge of carbon, such as graphite, laser ablation, etc., or its organic solvent from the solution contained with an impurity It is the approach of carrying out separation recovery of the fullerene C60 of a high grade efficiently, and moreover, actuation and a process are easy, a space time yield is large, and it is fully in offering the practically remarkable useful purification approach of fullerene C60 easily applicable also to mass production method of industrial magnitude.

[0010]

[Means for Solving the Problem] As opposed to the solution which contains with an impurity the fullerene C60 extracted from the fullerene C60 content soot obtained by various kinds of approaches using the suitable organic solvent as a result of repeating research wholeheartedly that this invention persons should attain said object By performing specific processing of making activated carbon contact, this impurity could be efficiently removed with activated carbon, and it found out that the fullerene C60 of a high grade could fully be obtained with sufficient yield by carrying out separation clearance of the organic solvent according to a conventional method from the obtained processing liquid. Moreover, this approach was easily applicable also to mass production method of the industrial magnitude of processing raw material soot and its extract efficiently to a large quantity, and since actuation was easy and there were also few processes, it turned out that it is the industrial very advantageous purification approach.

[0011] Based on the above knowledge, this invention persons came to complete this invention. That is, from the soot containing fullerene C60, this invention offers the purification approach of the fullerene C60 characterized by carrying out separation clearance of the organic solvent from the obtained processing liquid, after carrying out contact processing of the solution which contains with an impurity the fullerene C60 extracted with

the organic solvent with activated carbon.

[0012] In the approach of this invention, it is more important than the soot containing fullerene C60 to carry out contact processing of the solution which contains with an impurity the fullerene C60 extracted with the organic solvent with activated carbon.

[0013] As the manufacture approach, especially a limit does not have fullerene C60 content soot (it may be hereafter called raw material soot) used here as a raw material of extract down stream processing by said organic solvent, and it can use what was manufactured by various kinds of approaches, such as a well-known approach. Specifically, the fullerene C60 content soot obtained by the arc discharge and laser ablation of graphite is used suitably. In addition, before presenting an organic solvent extract, pretreatment of ether washing processing for example, etc. may be suitably performed to the raw material soot containing such fullerene C60 if needed. Moreover, mixing what was manufactured according to an approach which could use these fullerene C60 content soot by the one-sort independent, or is different, or conditions etc. may use two or more sorts together as mixture etc.

[0014] Although various kinds of organic solvents (an independent solvent or mixed solvent) are usable if it has sufficient solubility from said raw material soot (fullerene C60 content soot) to fullerene C60 as said organic solvent used for the extract of fullerene C60 (crude fullerene C60) as extractant, aromatic hydrocarbon, such as benzene, toluene, a xylene, and a mesitylene, etc. is usually used suitably. In addition, these aromatic hydrocarbon can be suitably used also as an one-sort independent solvent or two or more sorts of mixed solvents. Moreover, these aromatic hydrocarbon solvents for an extract can also be used where other components, such as other organic solvents, are contained in the range which does not check the object of this invention.

[0015] it is independent about various kinds of approaches, such as a continuous extraction method there is especially no limit also as this extract approach, and can adopt various kinds of extract approaches, such as a well-known approach, for example, according to a Soxhlet extraction method and heating application of pressure, — it is — it can be used, combining suitably.

[0016] In this way, the organic solvent extract collected from the extract process is a solution of the crude fullerene C60 which contains various kinds of impurities (for example, fullerene other than fullerene C60, carbon or a carbon compound of other gestalten, etc.) with fullerene C60.

[0017] Contact processing with activated carbon is presented with the solution which contains with an impurity the fullerene C60 extracted with the organic solvent in this way in the approach of this invention.

[0018] Although the extract itself obtained by said organic solvent extract is usually suitably used as a solution (the crude fullerene solution with which this activated carbon treatment is presented may be hereafter called a raw material solution) with which contact processing with this activated carbon is presented, the solution which performed adjustment of concentration or a presentation suitably to this extract depending on the case is also used suitably.

[0019] Of course, the crude fullerene C60 obtained from the extract obtained as mentioned above by carrying out separation clearance of the organic solvent may be again dissolved in suitable solvents, such as said aromatic hydrocarbon, and contact processing with said activated carbon may be presented with the solution. That is, when the fullerene C60 which could present contact processing with said activated carbon with the solution, and was extracted with the organic solvent as was the above beforehand when the crude fullerene C60 (powder etc.) beforehand obtained by the extract by the organic solvent was available, and the solution included with an impurity are available, contact processing with activated carbon can be presented with this. Thus, when the extract processing by the organic solvent is already made, the extract process by said organic solvent can be skipped.

[0020] The aromatic hydrocarbon system solvent which makes a principal component above mentioned aromatic hydrocarbon or this above mentioned as a solvent in the solution

(solution which contains fullerene C60 with an impurity) with which contact processing with said activated carbon is presented is used suitably. That is, in the approach of this invention, since the continuous method of presenting contact processing with activated carbon with the extract obtained from that extract process, using an aromatic hydrocarbon (system) solvent as said solvent for an extract can adopt suitably, it has the advantage that a process can be remarkably simplified also in this point.

[0021] As said activated carbon, various kinds of things, such as activated carbon of animal systems, such as activated carbon of vegetable systems, such as minerals, such as a coal system and a petroleum system, or activated carbon of a mineral oil system, and a thing of a charcoal system, coconut shell charcoal, and bone charcoal, are usable. Also in these, the activated carbon of a mineral oil system or a vegetable system is usually used suitably.

There is especially no limit also as the configuration of activated carbon, and a particle size, for example, anythings, such as a thing of the shape of powder and a grain, are usable. What is necessary is just to select the configuration and particle size suitably in consideration of contacting efficiency, the effectiveness of a subsequent separation process, etc. In addition, these activated carbon of various kinds of may be used by the one-sort independent, and can also mix and use two or more sorts together.

[0022] As contact mode of processing of said solution and activated carbon, there is especially no limit and various kinds of mode of processing can apply it. Usually, the method processed by adding and stirring activated carbon in said solution, for example is adopted suitably. that time -- processing temperature -- usually -- ordinary temperature -- it is good to set [ 200-degree C ] it as the temperature of the range of ordinary temperature -100 degree C preferably. As a system pressure in this processing, there is especially no limit and, in ordinary pressure or self-\*\* of a processor, application of pressure, etc., all can adopt it. That is, the bottom of ordinary temperature ordinary pressure, heating ordinary pressure, heating application of pressure, and ordinary temperature application of pressure etc. can carry out contact processing with this activated carbon on condition that versatility.

Although the processing time for fully performing this activated carbon treatment cannot be uniformly defined since it changes with other conditions, such as a class of activated carbon, the amount used, and processing conditions, processing of for [ 1 minute ] - about 2 hours is usually enough as it.

[0023] In addition, said activated carbon treatment is not limited to the method which uses the above activated carbon in the state of suspension, and other methods, such as a method which circulates said solution to this, using activated carbon as the fixed bed etc., can perform it suitably.

[0024] It is appropriate for the amount of the activated carbon used to usually select 0.01-100g in the range of 0.05-10g preferably to 1g of solutes in the solution with which processing is presented. an impurity tends to remain in the processing liquid which it became being less than 0.01g per 1g of solutes in the solution to process removing [ of the impurity from this solution ] the amount of the activated carbon used (adsorption treatment by activated carbon) inadequate, therefore was obtained, and the object of this invention is fully boiled and it becomes impossible here, to attain it On the other hand, when the amount of the activated carbon used exceeds 100g per 1g of solutes in the solution to process, it becomes impossible to disregard the amount of adsorption to the activated carbon of the fullerene C60 in this solution, and the yield (recovery) of the desired fullerene C60 may fall.

[0025] As mentioned above, by carrying out contact processing of the solution which contains with an impurity the fullerene C60 obtained by organic solvent extract with activated carbon, activated carbon is selectively adsorbed in the impurity in this solution, therefore the solution after this activated carbon treatment turns into a solution of the fullerene C60 of a high grade with which the fullerene C60 in a raw material solution was left behind almost as it was.

[0026] In the approach of this invention, after performing contact processing with activated carbon as mentioned above, separation clearance of the activated carbon (activated carbon

which adsorbed the impurity) is carried out that fullerene C60 solutions of the high grade which is the processed solution should be collected from the product. Separation of this activated carbon and the processed solution can be easily performed by various kinds of approaches, such as a well-known approach.

[0027] For example, when a suspension method performs said activated carbon treatment, separation clearance of said activated carbon can be suitably performed with a filtration process, a centrifuge method, etc. The separation approach by filtration is used especially suitably. Separation by this filtration can be easily performed according to a conventional method, for example, it can carry out with the application of various kinds of filtration methods, such as ordinary temperature ordinary pressure filtration, heating ordinary pressure filtration, heating pressure filtration, ordinary temperature pressure filtration, ordinary temperature filtration under reduced pressure, and heating filtration under reduced pressure. In the case of the negotiation method using activated carbon as the fixed bed, although it dissociates automatically, activated carbon and processing liquid should just remove this particle with a filtration process etc. as mentioned above, when solid-state particles, such as activated carbon, mix into recovery liquid in this case.

[0028] In addition, generally the fullerene C60 of a minute amount has adhered to the activated carbon separated by filtration etc. as mentioned above with the solvent. Then, in order to raise the recovery of fullerene C60 more, washing this activated carbon with the suitable solvent for washing that the adhering fullerene C60 should be collected is also performed suitably. These washing recovery liquid may be mixed, packed and collected in said separation recovery liquid.

[0029] As this solvent for washing, said aromatic hydrocarbon (system) solvents, such as benzene, toluene, a xylene, and a mesitylene, are usually used suitably. Although this solvent for washing may not be the not necessarily same class as the solvent which constitutes the solution with which activated carbon treatment was presented, and the thing of a presentation, when the effectiveness of the whole process, such as improvement in the profitability by the recycle activity of a solvent, is taken into consideration, the same thing is used suitably. For example, after presenting said activated carbon treatment with the toluene solution obtained at the extract process, using toluene as said solvent for an extract, the approach of washing the separated activated carbon with toluene can be especially illustrated as a desirable mode.

[0030] Separation recovery of the processing liquid (solution of the fullerene C60 of a high grade) from which the impurity was selectively and fully removed by activated carbon treatment as mentioned above can be carried out efficiently.

[0031] In the approach of this invention, the fullerene C60 refined by the high grade is obtained from the processing liquid (solution of the fullerene C60 of a high grade) by which separation recovery was carried out as mentioned above from the activated-carbon-treatment process by carrying out separation clearance of the organic solvent. Although separation clearance of the organic solvent from this processing liquid can be performed by various approaches, according to a conventional method, the approach of distilling [ atmospheric distillation / vacuum distillation, ] off an organic solvent by vacuum distillation preferably is usually suitably adopted from this solution. Thus, by distilling off an organic solvent, the solid-state-like (shape of crystal) purification fullerene C60 is obtained as the residue. Although the purification fullerene C60 obtained is obtained where about several% of solvent is contained during a crystal depending on extent of desiccation, the purification fullerene C60 said by this invention may contain the solvent of a minute amount in this way. Of course, if needed, it may be made to dry suitably and a solvent may fully be removed. that is, separation clearance of said organic solvent or desiccation of the purification fullerene C60 is not necessarily performed thoroughly — also coming out — it is good and can acquire as purification fullerene C60 of various aridity according to the purpose of using a product etc. Moreover, extent of separation clearance of an organic solvent can be adjusted by the case, it can collect as the various solutions or the dispersion liquid of the purification

fullerene C60 of concentration, this can also be used as a product by the approach of this invention, and the solution of the purification fullerene C60 of a high grade collected after said activated carbon treatment can also be further used as an intermediate product in the approach of this invention.

[0032] Moreover, the purification fullerene C60 which carried out separation clearance and obtained the organic solvent is recrystallized, and can also be further made into the purification fullerene C60 of a high grade.

[0033] As mentioned above, at best [ yield ] moreover, easy actuation and an easy process can recover efficiently the fullerene C60 refined by the high grade from the raw material soot (or solution of the crude fullerene C60 by which the organic solvent extract was already carried out) which contains fullerene C60 by the purification approach of this invention. Moreover, since the fullerene C60 refined by altitude since it consisted of processes to which all were suitable for the mass-production method, such as solvent separation of solvent extraction, activated carbon treatment, solvent distilling off, etc., in the case of the approach of this invention can also be mass-produced easily, as compared with the purification method using the conventional column separation for example, etc., it is remarkably advantageous industrially.

[0034] The purification fullerene C60 (or the solution) obtained by the approach of this invention can be used suitable for various kinds of fullerene C60 fields of the invention including the electrical and electric equipment and the electronic field, such as a raw material of an electrical conducting material and a superconductor. In that case, this purification fullerene C60 can respond in activity eye, and can be used with various gestalten, such as mixture with the powder (crystal) of various aridity, a solution, dispersion liquid, and other matter of various kinds of, and a constituent.

[0035]

[Example] Although the example of this invention explains this invention more concretely below, this invention is not limited to these examples.

As example 1 raw-material soot, using the fullerene C60 content soot obtained by the arc discharge of graphite, extract processing of this soot 5g was carried out with 1l. toluene using the Soxhlet extractor, and the extract was obtained. The obtained extract whole quantity was condensed, it considered as the 500ml solution, 20g (Wako Pure Chem make) of activated carbon powder was added in this solution, and it processed for 15 minutes under heating stirring at 70 degrees C. From the obtained processing mixed liquor, by filtration, separation clearance of the activated carbon was carried out, the activated carbon of filtration was washed several times with a small amount of toluene, and washingses were mixed and collected to filtrate. The toluene of a solvent was distilled out of this recovery liquid using the evaporator, and the purification object which is dried at 100 degrees C for 12 hours, and targets obtained residue under a vacuum was obtained. Yield was 260mg. When the mass spectrum analyzed this obtained purification object, only the peak peculiar to C60 of a natural isotope presentation, such as peak  $[M+=720$  (12C60) originating in C60,  $M+=721$  (12C5913C1),  $M+=722$  (12C5813C2), and  $M2+=360$  (12C60), was observed. Moreover, in 13 C-NMR analysis, the characteristic peak was observed by 143.2 ppm C60. From these results etc., it was checked that the purification object with which the above was obtained is the pure fullerene C60.

[0036] In example 2 example 1, the purification object was obtained like the example 1 except having set the addition of activated carbon to 5g, and having made heating mixing time into 2 hours. Yield was 160mg. The same mass spectrum as the purification object which also obtained this purification object in the example 1, and the NMR spectrum were shown, and it was checked that this is the pure fullerene C60.

[0037] Extract processing of the same raw material soot 5.0g as what was used in the example of comparison 1 example 1 was carried out with toluene like the example 1, and the extract was obtained. When the solvent was distilled out of this extract, 450mg of soot-like objects which use fullerene C60 as a principal component, and contain an impurity was



obtained.

[0038] Next, the neutral alumina was made into the separating medium for this obtained soot-like object (crude fullerene C60), column chromatography separation was performed by having used the hexane as the expansion solvent, and the fraction equivalent to fullerene C60 was isolated preparatively. The solvent was distilled out of this preparative isolation liquid, and 380mg of purification objects was obtained. This purification object gave the result of the same mass spectrum as the purification object obtained in the example 1, and <sup>13</sup>C-NMR, and it was checked that it is the pure fullerene C60 similarly.

[0039] In addition, the time amount from which the amount of the neutral alumina used in the case of the above-mentioned column chromatography separation is 21l., and separation took the amount of 3kg and the expansion solvent used to it was 12 hours. Thus, in the case of the purification method by the column chromatography separation which is a conventional method, a lot of separating media and expansion solvents were needed also to little purification, the operate time was also long, to mass production method, it is unsuitable, and it was industrially checked that it is disadvantageous as it generally said from the former.

[0040] On the other hand, it can carry out isolation purification of the fullerene C60 of a high grade in a short time, and since industrial large quantity processing is easy for the purification approach using the activated carbon treatment of this invention etc. through all processes, it is suitable as the industrial purification approach, so that the above-mentioned examples 1 and 2 may also show easily.

[0041]

[Effect of the Invention] As opposed to the solution of the crude fullerene C60 which was extracted with the organic solvent by the conventional method etc. from the fullerene C60 content soot obtained by the arc discharge of carbon, such as graphite, laser ablation, etc. according to the approach of this invention Since the specific method of performing activated carbon treatment and carrying out adsorption treatment of the impurity selectively is used Extremely, separation recovery can be efficiently carried out with recovery high enough, and moreover, since actuation and a process are easy and a space time yield is also large, the fullerene C60 of a high grade is easily applicable also to mass production method of industrial magnitude. That is, according to this invention, the purification approach of the advantageous fullerene C60 remarkable as the industrial purification approach for obtaining the fullerene C60 of a high grade can be offered.

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(54)【発明の名称】 フラーレンC<sub>60</sub>の精製方法

(57)【要約】

【目的】 グラファイト等の炭素のアーカ放電、レーザーアブレーションなどによって得られたスス等のフラーレンC<sub>60</sub>を含有するススやその有機溶媒による抽出により得られたフラーレンC<sub>60</sub>を不純物とともに含有する溶液から、十分に高純度のフラーレンC<sub>60</sub>を、効率よく分離回収する方法であって、しかも、操作及び工程が簡単で、空時収率が大きく、工業的規模の大量生産にも容易に適用することができる実用上著しく有用な、フラーレンC<sub>60</sub>の精製方法を提供する。

【構成】 フラーレンC<sub>60</sub>を含有するススより、有機溶媒により抽出したフラーレンC<sub>60</sub>を不純物とともに含む溶液を、活性炭と接触処理した後、得られた処理液より有機溶媒を分離除去することによりフラーレンC<sub>60</sub>を精製する。

を提供することにある。

#### 【0010】

【課題を解決するための手段】本発明者らは、前記目的を達成すべく鋭意研究を重ねた結果、各種の方法によって得られたフラレーンC<sub>60</sub>含有ススから、適当な有機溶媒を用いて抽出したフラレーンC<sub>60</sub>を不純物とともに含む溶液に対して、活性炭に接触させるという特定の処理を施すことによって該不純物を活性炭とともに効率よく除去することができ、得られた処理液から常法に従って有機溶媒を分離除去することによって十分に高純度のフラレーンC<sub>60</sub>を収率よく得ることができることを見出した。また、この方法は、原料ススやその抽出液を大量に効率よく処理するという工業的規模の大量生産にも容易に適用することができ、しかも、操作が簡単で工程も少ないので工業的に極めて有利な精製方法であることが分かった。

【0011】以上の知見に基づいて、本発明者らは、本発明を完成するに至った。すなわち、本発明は、フラレーンC<sub>60</sub>を含有するススより、有機溶媒により抽出したフラレーンC<sub>60</sub>を不純物とともに含む溶液を、活性炭と接触処理した後、得られた処理液より有機溶媒を分離除去することを特徴とするフラレーンC<sub>60</sub>の精製方法を提供するものである。

【0012】本発明の方法においては、フラレーンC<sub>60</sub>を含有するススより、有機溶媒により抽出したフラレーンC<sub>60</sub>を不純物とともに含む溶液を、活性炭と接触処理することが重要である。

【0013】ここで、前記有機溶媒による抽出処理工程の原料として使用されるフラレーンC<sub>60</sub>含有スス（以下、原料ススと呼ぶことがある。）は、その製造方法としては特に制限はなく、公知の方法等の各種の方法によって製造されたものを使用することができる。具体的には、例えば、グラファイトのアーカ放電やレーザーアブレーションにより得られたフラレーンC<sub>60</sub>含有スス等が好適に使用される。なお、これらのフラレーンC<sub>60</sub>を含有する原料ススには、有機溶媒抽出に供する前に必要に応じて適宜、例えばエーテル洗浄処理等の前処理が施されてもよい。また、これらのフラレーンC<sub>60</sub>含有ススは、1種単独で使用してもよく、あるいは異なった方法や条件によって製造されたものを混合するなど2種以上を混合物等として併用してもよい。

【0014】前記原料スス（フラレーンC<sub>60</sub>含有スス）からフラレーンC<sub>60</sub>（粗製フラレーンC<sub>60</sub>）の抽出に抽出剤として使用する前記有機溶媒としては、フラレーンC<sub>60</sub>に対して十分な溶解性を有するものであれば各種の有機溶媒（単独溶媒又は混合溶媒）が使用可能であるが、通常は、例えば、ベンゼン、トルエン、キシレン、メシチレン等の芳香族炭化水素などが好適に使用される。なお、これらの芳香族炭化水素は、1種単独溶媒としても、あるいは2種以上の混合溶媒としても好適に使

用することができる。また、これらの抽出用芳香族炭化水素溶媒は、本発明の目的を阻害しない範囲で、他の有機溶媒等の他の成分を含有した状態で使用することもできる。

【0015】この抽出方法としても、特に制限はなく、公知の方法等の各種の抽出方法が採用可能であり、例えば、ソックスレー抽出法、加熱加圧による連続抽出法等の各種の方法を単独であるいは適宜組み合わせ使用することができる。

10 【0016】こうして抽出工程から回収された有機溶媒抽出液は、フラレーンC<sub>60</sub>とともに各種の不純物（例えば、フラレーンC<sub>60</sub>以外のフラレーン類や他の形態の炭素類もしくは炭素化合物等）を含有している粗製のフラレーンC<sub>60</sub>の溶液である。

【0017】本発明の方法においては、このように有機溶媒により抽出されたフラレーンC<sub>60</sub>を不純物とともに含む溶液を活性炭との接触処理に供する。

20 【0018】この活性炭との接触処理に供する溶液（以下、この活性炭処理に供する粗製フラレーン溶液を原料溶液と呼ぶことがある。）としては、通常は、前記有機溶媒抽出によって得た抽出液そのものが好適に使用されるが、場合によっては、該抽出液に対して適宜濃度や組成の調整を行った溶液も好適に使用される。

30 【0019】もちろん、上記のようにして得た抽出液から有機溶媒を分離除去して得られた粗製のフラレーンC<sub>60</sub>を再び前記芳香族炭化水素等の適当な溶媒に溶解し、その溶液を前記活性炭との接触処理に供してもよい。すなわち、予め有機溶媒による抽出によって得られた粗製のフラレーンC<sub>60</sub>（粉末等）が入手可能な場合には、その溶液を前記活性炭との接触処理に供してもよく、また、予め前記のようにして有機溶媒によって抽出されたフラレーンC<sub>60</sub>と不純物とともに含む溶液が入手可能な場合には、これを活性炭との接触処理に供することができる。このように有機溶媒による抽出処理がすでになされている場合には、前記有機溶媒による抽出工程を省略することができる。

40 【0020】前記活性炭との接触処理に供する溶液（フラレーンC<sub>60</sub>を不純物とともに含む溶液）における溶媒としては、前記した芳香族炭化水素もしくはこれを主成分とする芳香族炭化水素系溶媒が好適に使用される。すなわち、本発明の方法においては、前記抽出用溶媒として芳香族炭化水素（系）溶媒を用い、その抽出工程から得られた抽出液を活性炭との接触処理に供するという連続方式が好適に採用することができるので、この点においても工程を著しく簡略化することができるという利点を有している。

50 【0021】前記活性炭としては、石炭系、石油系等の鉱物もしくは鉱油系の活性炭、木炭系のものやヤシガラ炭等の植物系の活性炭、骨炭等の動物系の活性炭など各種のものが使用可能である。これらの中でも、通常は、

溶媒を十分に除去してもよい。すなわち、前記有機溶媒の分離除去もしくは精製フラーレンC<sub>60</sub>の乾燥は必ずしも完全に行わないでもよく、製品の使用目的等に応じて種々の乾燥度の精製フラーレンC<sub>60</sub>として取得することができる。また、場合によっては、有機溶媒の分離除去の程度を調節して、種々の濃度の精製フラーレンC<sub>60</sub>の溶液又は分散液として回収し、これを本発明の方法による製品として利用することもできるし、さらには、前記活性炭処理後回収された高純度の精製フラーレンC<sub>60</sub>の溶液を、本発明の方法における中間製品として利用することもできる。

【0032】また、有機溶媒を分離除去して得た精製フラーレンC<sub>60</sub>を、再結晶して、さらに高純度の精製フラーレンC<sub>60</sub>とすることもできる。

【0033】以上、本発明の精製方法によって、フラーレンC<sub>60</sub>を含有する原料スス（あるいは、すでに有機溶媒抽出された粗製フラーレンC<sub>60</sub>の溶液）から、高純度に精製されたフラーレンC<sub>60</sub>を収率よく、しかも簡単な操作及び工程によって効率よく回収することができる。また、本発明の方法の場合、溶媒抽出、活性炭処理、溶媒留去等の溶媒分離等のいずれも大量生産方式に適した工程からなっているので、高度に精製されたフラーレンC<sub>60</sub>を容易に大量生産することもできるので、例えば、従来のカラム分離を用いる精製法等と比較して工業的に著しく有利である。

【0034】本発明の方法によって得られた精製フラーレンC<sub>60</sub>（あるいは、その溶液）は、例えば、導電材料、超伝導体の素材など、電気・電子分野をはじめとする各種のフラーレンC<sub>60</sub>利用分野に好適に使用することができる。その際、この精製フラーレンC<sub>60</sub>は、使用目的に応じて、種々の乾燥度の粉末（結晶）、溶液、分散液、他の各種の物質との混合物や組成物等の種々の形態で利用することができる。

#### 【0035】

【実施例】以下に、本発明の実施例によって本発明をより具体的に説明するが、本発明はこれらの実施例に限定されるものではない。

#### 実施例1

原料ススとして、グラファイトのアーキ放電によって得られたフラーレンC<sub>60</sub>含有ススを用い、該スス5gをソックスレー抽出器を用いて1リットルのトルエンで抽出処理して抽出液を得た。得られた抽出液全量を濃縮して500mlの溶液とし、該溶液に活性炭粉末（和光純薬社製）20gを添加し、70℃に加熱攪拌下で15分間処理した。得られた処理混合液より、濾過によって活性炭を分離除去し、濾過の活性炭を少量のトルエンで数回洗浄し、洗液を濾液に混合して回収した。この回収液からエバポレーターを用いて溶媒のトルエンを留去し、得られた残渣を真空下、100℃で12時間乾燥させ目的とする精製物を得た。収量は260mgであった。この

得られた精製物をマスペクトルで分析したところC<sub>60</sub>に由来するピーク [M<sup>+</sup> = 720 (<sup>12</sup>C<sub>60</sub>)、M<sup>+</sup> = 721 (<sup>12</sup>C<sub>59</sub><sup>13</sup>C<sub>1</sub>)、M<sup>+</sup> = 722 (<sup>12</sup>C<sub>58</sub><sup>13</sup>C<sub>2</sub>)、M<sup>+</sup> = 360 (<sup>12</sup>C<sub>30</sub>) など天然同位元素組成のC<sub>60</sub>に特有のピーク) のみが観察された。また、<sup>13</sup>C-NMR分析では、143.2ppmにC<sub>60</sub>に特有のピークが観察された。これらの結果等から、上記の得られた精製物が純粋なフラーレンC<sub>60</sub>であることが確認された。

#### 【0036】実施例2

実施例1において、活性炭の添加量を5gとし、かつ、加熱攪拌時間を2時間とした以外は、実施例1と同様にして精製物を得た。収量は160mgであった。この精製物も実施例1で得た精製物と同様のマスペクトル及びNMRスペクトルを示し、これが、純粋なフラーレンC<sub>60</sub>であることが確認された。

#### 【0037】比較例1

実施例1で用いたものと同じ原料スス5.0gを実施例1と同様にしてトルエンで抽出処理し、抽出液を得た。この抽出液から溶媒を留去したところフラーレンC<sub>60</sub>を主成分とし不純物を含むスス状物が450mg得られた。

【0038】次に、この得られたスス状物（粗製のフラーレンC<sub>60</sub>）を、中性アルミナを分離剤とし、ヘキサンを展開溶媒として、カラムクロマト分離を行い、フラーレンC<sub>60</sub>に相当するフラクションを分取した。この分取液から溶媒を留去し、精製物を380mg得た。この精製物は、実施例1で得た精製物と同様のマスペクトル及び<sup>13</sup>C-NMRの結果を与え、同様に純粋なフラーレンC<sub>60</sub>であることが確認された。

【0039】なお、上記カラムクロマト分離の際の中性アルミナの使用量は3kg、展開溶媒の使用量は21リットルであり、分離に要した時間は12時間であった。このように、従来法であるカラムクロマト分離による精製法の場合は、少量の精製に対しても多量の分離剤や展開溶媒を必要とし、操作時間も長く、従来から一般に言われているように、大量生産には不適當であり、工業的には不利であるということが確認された。

【0040】これに対して、上記実施例1及び2からも容易にわかるように、本発明の活性炭処理等を用いる精製方法は、短時間で高純度のフラーレンC<sub>60</sub>を単離精製することができ、全工程を通して工業的大量処理が容易であるので、工業的な精製方法として好適である。

#### 【0041】

【発明の効果】本発明の方法によると、グラファイト等の炭素のアーキ放電、レーザーアブレーション等によって得られたフラーレンC<sub>60</sub>含有ススより従来法等によって有機溶媒で抽出された粗製のフラーレンC<sub>60</sub>の溶液に対して、活性炭処理を行い不純物を選択的に吸着除去するという特定の方法を用いているので、極めて高純度の